LIQUID STABILIZER COMPRISING METAL SOAP AND SOLUBILIZED METAL PERCHLORATE

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Abstract

A liquid stabilizer suitable for use in a vinyl chloride polymer comprising a liquid mixture of metal soap stabilizer, for example, a mixture of a mixed barium/zinc soap stabilizer and solubilized metal perchlorate, for example, a barium perchlorate. The liquid stabilizer is formed by combining a solubilized metal perchlorate and a liquid mixture of the metal soap stabilizer.

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(57) Abstract

A liquid stabilizer suitable for use in a vinyl chloride polymer comprising a liquid mixture of metal soap stabilizer, for example, a mixture of a mixed barium/zinc soap stabilizer and solubilized metal perchlorate, for example, a barium perchlorate. The liquid stabilizer is formed by combining a solubilized metal perchlorate and a liquid mixture of the metal soap stabilizer.

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LIQUID STABILIZER COMPRISING METAL SOAP AND SOLUBILIZED METAL PERCHLORATE

BACKGROUND OF THE INVENTION

Vinyl halide polymers, particularly polyvinyl chloride resins, are used in a variety of applications. These thermoplastic polymers can be fabricated into useful articles by extrusion, injection molding, compression molding and other thermoforming methods. To stabilize vinyl halide polymers during thermoforming methods, heat or thermal stabilizers and co-stabilizers are added to the resins. Examples of known stabilizers include organometallic stabilizers, mixed metallic stabilizers, and inorganic stabilizers. Metallic stabilizers include heavy metal, alkali metal and alkaline earth metal salts of fatty acids. The heavy metals include lead, cadmium, tin and zinc. Examples of mixed metallic stabilizers include fatty acid salts of zinc and calcium, zinc and barium, barium and cadmium, lead and barium, or two or more of other metals. Examples of inorganic stabilizers include lead carbonate, lead sulfate, and mixtures of tribasic lead sulfate and dibasic lead stearate. Examples of organic, non-metallic stabilizers or co-stabilizers include epoxidized soybean oil, tris nonylphenyl phosphite, beta diketones, and phenylindole.

Stabilization of polyvinyl chloride has also been addressed in cases where organic nitrogen-induced degradation becomes a problem such as in applications in which polyvinyl chloride is affixed to a urethane foam backing. The residual amine catalyst in the polyurethane is the degradation catalyst.

Among the references pertinent to this general area of technology are the following:

1. U.S. Patent No. 5,034,443 to K. Bae et al. describes stabilizer compositions which are free-flowing powder compositions and which contain blends of sodium perchlorate hydrate and calcium silicate. This patent also describes a solution of sodium perchlorate in water with calcium silicate and a non-absorbing diluent powder, such as calcium carbonate, to provide a "free-flowing powder composition".

2. U.S. Patent No. 4,861,816 to M. Kobayashi describes a solid stabilizer mixture of a barium salt of a carboxylic acid and a zinc salt of a carboxylic acid, each having a melting point of no lower than 250°C, with a metal perchlorate and/or perchlorate ion type hydrotalcite compound.

3. U.S. Patent No. 4,957,954 to S. Iizuka et al. describes a stabilizer comprising a 2,2,6,6-tetramethyl piperidinyl compound and an ammonium or metal perchlorate.

4. Japanese Patent Publication No. 61/272,258 describes heat stabilizers containing a predominant amount of organic tin compounds with lower amounts of hydrotalcites and still generally lower levels of barium perchlorate.

5. Japanese Patent Publication No. 04/50,250 describes solid powder stabilizers comprising Group IA metal salts of perchloric acid, hydrotalcite and/or zeolites, and organic powder.

6. Japanese Patent Publication No. 04/183,735 describes use of compositions comprising organic acid salt(s) of (1) sodium, potassium, magnesium, calcium, barium, and zinc and alkyltin compounds; (2) sulpholene compounds; and (3) β-diketone compounds of a certain formula or their sodium, magnesium, calcium, barium or zinc salts.

SUMMARY OF THE INVENTION

A liquid stabilizer suitable for use in a vinyl chloride polymer comprising a homogeneous, clear liquid mixture of at least one metal soap stabilizer and a solubilized metal perchlorate. The liquid stabilizer is formed by combining a solubilized metal perchlorate and a liquid mixture of at least one metal soap stabilizer. The stabilizer composition of this invention can be used at from about 0.5 weight part to about 10 weight parts per 100 parts by weight of polyvinyl chloride. It provides excellent protection against thermal degradation and coloration when exposed to polyurethane foam.

DESCRIPTION OF PREFERRED EMBODIMENTS

One major component of the composition of the present invention is what might be termed a "metal soap stabilizer" component. Such compositions are known to persons of ordinary skill in the art and comprise one or more metal salts of a carboxylic acid. For example, there can be used salts of saturated and unsaturated higher fatty acids having 6 to 22 carbon atoms, especially 8 to 18 carbon atoms, with the metals of Groups IIA and IIB of the Periodic Table, for example, the Ca, Ba, Mg and Zn salts of the above-mentioned fatty acids, especially of such acids as palmitic acid, stearic acid, oleic acid, lauric acid, coconut oil fatty acid, and palm oil fatty acid, being preferably used. These metal salts are generally used in the form of mixtures of two or more of them.

The second major component is a solubilized metal perchlorate. The metal may be selected from metals from Group IA (e.g., sodium or potassium), Group IIA (e.g., barium or magnesium), Group IIIA (e.g., aluminum), Group IVA (e.g., tin or lead), or Group IIB (e.g., zinc or cadmium) of the

Periodic Table of the Elements. Mixtures of such perchlorates can be used, if desired. Solubilization of the perchlorate is preferably achieved by using a relatively high boiling polar oxygenated solvent so as not to contribute to fogging problems when the stabilizer is used in a plasticized vinyl chloride polymer under high temperature conditions. Ethers and hydroxy-containing solvents meeting these requirements are representative. Representative solvents include tripropylene glycol, butylcarbitol, triethylene glycol, and butylene glycol. This composition can also contain conventional antioxidants, metal chelators, lubricants, color improvers, and other functional additives known to persons in the art of polymer stabilization.

The relative weight amounts of mixed metal soap component to solubilized metal perchlorate component (metal perchlorate and solvent for the metal perchlorate) in the novel stabilizer of the present invention can range from about 20:1 to about 5:1 on a weight basis, preferably from about 10:1 to about 6:1.

The present invention is further understood by the Examples which follow.

EXAMPLES 1-8

A series of eight liquid barium-zinc stabilizer-containing compositions were prepared as further described in the Table given below.

The barium-zinc portion of the stabilizer compositions were first formed by mixing the indicated amounts of dipolypropylene glycol phenyl phosphite (DHOP), diisodecyl pentaerythritol diphosphite (WESTON 600 brand), nonyl phenol, and zinc 2-ethylhexanoate (CAR ZIN 18 Brand, 18% zinc). The mixture was heated to 70°C with agitation. Benzoic acid was then added and agitation was continued until the components dissolved. Then, 5 gm of barium nonyl phenate-carbonate complex (overbased-28% barium) BNP 28HF (Special) brand, was added. Agitation was continued until foaming ceased and the remaining amount of the barium material was added. Then the indicated amount of oleic acid was added and agitation was continued until any evidence of foaming ended. Then, dibenzoylmethane (RHODIASTAB 83 brand, abbreviated below as "RH-83") and mineral spirits was added.

The barium perchlorate portion of the stabilizer was formed by mixing 20 gm of barium perchlorate and 80 gm of tripropylene glycol and heating the resulting mixture to 80°C until dissolution of the barium perchlorate had been achieved.

The final step involved addition of the liquid barium perchlorate-tripropylene glycol (TPG) composition to the liquid barium-zinc stabilizer composition and the mixture was heated to 80°C and agitated until dissolution of any solid material was achieved.

The Table sets forth the ingredients used in formulating the compositions and the percent barium, zinc, phosphorus, and barium perchlorate in each:

TABLE

Materials	1	2	3	4
DHOP	25.0	29.0	27.0	26.0
Weston 600	4.0	4.0	4.0	4.0
Nonyl Phenol	3.0	3.0	3.0	3.0
Car Zin 18	12.0	12.0	12.0	12.0
Benzoic Acid	2.0	2.0	2.0	2.0
BNP 28H (Special)	42.9	42.9	42.9	42.9
Oleic Acid	4.0	4.0	4.0	4.0
RH-83	1.6	1.6	1.6	1.6
Mineral Spirits	1.5	1.5	1.5	1.5
$Ba(ClO_4)_2$/TPG 20% wt/wt	4.0	-	2.0	3.0
%Ba	12.01	12.01	12.01	12.01
%Zn	2.16	2.16	2.16	2.16
%P	3.38	3.85	3.61	3.49
$\%BaClO_4$	0.8	0	0.4	0.6

Materials	5	6	7	8
DHOP	28.0	33.0	27.0	31.0
Weston 600	4.0	4.0	4.0	4.0
Nonyl Phenol	3.0	3.0	3.0	3.0
Car Zin 18	10.0	10.0	10.0	10.0
Benzoic Acid	2.0	2.0	2.0	2.0
BNP 28H (Special)	42.9	35.7	35.7	35.7
Oleic Acid	4.0	4.0	4.0	4.0
RH-83	1.6	1.6	1.6	1.6
Mineral Spirits	1.5	2.7	2.7	2.7
$Ba(ClO_4)_2$/TPG 20% wt/wt	3.0	4.0	10.0	6.0
%Ba	12.01	10.0	10.0	10.0
%Zn	1.8	1.8	1.8	1.8
%P	3.73	4.33	3.85	4.09
$\%BaClO_4$	0.6	0.8	2.0	1.2

In the foregoing Table the following abbreviations are used to identify certain materials which were employed:

DHOP - Dipolypropylene glycol Phenyl Phosphite. This functions as an antioxidant and chelating agent for the zinc 2-ethylhexanoate to be listed below.

"Weston 600" - Diisodecyl Pentaerythritol Diphosphite. This also functions as an antioxidant and zinc chelator.

"Car Zin 18" - Zinc 2-Ethylhexanoate, 18% Zn. This is one of the primary metal soap stabilizers.

"BNP 28 HP" - Barium Nonyl Phenate, Carbonate Complex, 28% Ba (overbased). This is the other primary metal soap stabilizer.

"RH-83" - "Rhodiastab 83" - Dibenzoylmethane. This is a beta-diketone metal chelator.

TPG - Tripropylene Glycol. This is the solvent for the metal perchlorate additive used herein.

EXAMPLES 9-24

These Examples illustrate evaluation of certain of the formulations described in Examples 1-8. In the evaluation results the samples from Examples 1-6, respectively, are designated "A" through "F", respectively. Sample B contained no perchlorate and is presented for comparative purposes.

The composition which was used in the test to be described hereinafter was formed of the following components:

Component	Parts by Weight
PVC suspension resin	100.0
Plasticizer (JAYFLEX 9-11 Brand)	80.0
Calcium carbonate	25.0
Antimony oxide	5.0
Epoxidized soybean oil	3.5
Zinc borate	2.5
Stabilizer*	1.5
Stearic acid	0.25

*This component is one of the "Samples" mentioned hereinbefore as further described below.

The test composition was formed by first mixing the resin and plasticizer at room temperature until homogeneous. Calcium carbonate and antimony oxide were then added and blended into the plasticized resin until homogeneity was achieved. The remaining ingredients were added and blended as previously described. The composition was then ready for testing.

Dynamic Heat Stability

The dynamic heat stability was tested by placing 57 gm of the total formulation to be tested in a BRABENDER PLASTICORDER apparatus operating at 180°C and 63 rpm for thirty minutes. The sample was judged to pass the test if it showed no change ("NC") in color or torque in the BRABENDER apparatus and if there was no evidence of compound degradation. The results observed were as follows:

Sample Tested	Result
A	NC
B	NC
C	NC
D	NC
E	NC
F	NC

Dynamic Mill Stability

The samples were tested for sixty minutes at 170°C on a two-roll mill. The results are given below. A standard barium/zinc stabilizer package has a dynamic mill stability of over 5.0 ΔE units as measured on a HUNTERLAB colorimeter:

Sample	Result (ΔE)
B	2.88
C	4.28
D	3.97
E	3.77
F	2.41

Oven Stability

The samples were tested for seventy-two hours at 120°C. The color was then rated on a scale of from "1" (slight

darkening) to "10" (black) with a standard barium/zinc control being "6".

Sample	Result
A	8
F	3.0

Amine Stain Resistance

The samples were placed in contact with polyurethane foam for seven days at 80°C to judge whether the sample showed evidence of amine staining. No evidence of staining indicated an excellent sample and was coded "1" whereas a sample which failed and which showed evidence of strong discoloration was coded "10".

Sample	Result
A	3
B	6
F	2

The foregoing Examples have been presented for illustrative purposes only and should not be considered in a limiting sense for that reason. The scope of protection sought is set forth in the claims which follow.

I Claim:

1. A liquid stabilizer suitable for use in a vinyl chloride polymer comprising a liquid mixture of (1) at least one metal soap stabilizer and (2) a solubilized metal perchlorate.

2. A stabilizer as claimed in Claim 1 wherein the perchlorate comprises a metal which is selected from the group consisting of a Group IA and Group IIA metal from the Periodic Table.

3. A stabilizer as claimed in Claim 1 wherein the perchlorate is a Group IIA metal perchlorate.

4. A stabilizer as claimed in Claim 1 wherein the metal perchlorate is solubilized in a glycol ether solvent.

5. A stabilizer as claimed in Claim 1 wherein the weight ratio of metal soap stabilizer to solubilized metal perchlorate ranges from about 20:1 to about 5:1.

6. A stabilizer as claimed in Claim 1 wherein the weight ratio of metal soap stabilizer to solubilized metal perchlorate ranges from about 10:1 to about 6:1.

7. A stabilizer as claimed in Claim 3 wherein the perchlorate is barium perchlorate.

8. A stabilizer as claimed in Claim 1 which comprises a mixture of barium and zinc soap stabilizers and a solubilized Group IIA metal perchlorate.

9. A stabilizer as claimed in Claim 8 wherein the Group IIA metal is barium.

10. A process for forming a liquid stabilizer suitable for use in a vinyl chloride polymer which comprises a mixture of at least one metal soap stabilizer and a metal perchlorate which process comprises combining a solubilized metal perchlorate and a liquid mixture of the metal soap stabilizer.

11. A process as claimed in Claim 10 wherein the perchlorate comprises a metal which is selected from the group consisting of a Group IA and Group IIA metal from the Periodic Table.

12. A process as claimed in Claim 10 wherein the perchlorate is a Group IIA metal perchlorate.

13. A process as claimed in Claim 10 wherein the metal perchlorate is solubilized in a glycol ether solvent.

14. A process as claimed in Claim 10 wherein the weight ratio of metal soap stabilizer to solubilized metal perchlorate ranges from about 20:1 to about 5:1.

15. A process as claimed in Claim 10 wherein the weight ratio of metal soap stabilizer to solubilized metal perchlorate ranges from about 10:1 to about 6:1.

16. A process as claimed in Claim 12 wherein the perchlorate is barium perchlorate.

17. A process as claimed in Claim 10 which comprises a mixture of barium and zinc soap stabilizers and a solubilized Group IIA metal perchlorate.

18. A process as claimed in Claim 17 wherein the Group IIA metal is barium.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/04086

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :C08K 5/09; C09K 15/32
US CL :524/395, 399, 400; 252/400.1, 400.52, 400.61
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 524/395, 399, 400; 252/400.1, 400.52, 400.61

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS: metal perchlorate, borium perchlorate, PVC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US, A, 5,004,776 (TADENUMA ET AL) 02 April 1991. See col. 3, line 58 to col. 4, line 29, synthesis Example 6, Table 1, col. 3, lines 22-26 and col. 4, lines 25-30.	1-4,7,10-13 16 ---------- 5,6,14,15
Y	US, A, 4,957,954 (IIZUKA ET AL) 18 September 1990. See Tables in cols. 22 and 25.	8,9,17,18
Y	US, A, 4,861,816 (KOBAYASHI ET AL) 29 August 1989. See Table 2.	8,9,17,18

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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